Supplement Information

The simultaneous purification of PM and NOx for diesel engine exhausts over a single 3DOM Ce$_{0.9-x}$Fe$_{0.1}$Zr$_x$O$_2$ catalyst

Ying Cheng, Jian Liu *, Zhen Zhao, Yuechang Wei, Weiyu Song, Chunming Xu

State Key Laboratory of Heavy Oil Processing, China University of Petroleum, Beijing 102249, China

* Corresponding author: Tel: 86-10-89732278. Fax: 86-10-69724721.

Email: liujian@cup.edu.cn

Number of Pages: 15

Number of Figures: 11

Number of Tables: 1
Table S1. Simultaneous NOx reduction and PM combustion over 3DOM catalysts (100 mg catalyst loosely mixed with 10 mg model PM; 1000 ppm NO, 1000 ppm NH3, 3 % O2 and balance N2 at a gas hourly space velocity of 25000 h⁻¹).

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Tm ⁹ (°C)</th>
<th>Tfull NO conversion ¹ (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CeO₂</td>
<td>422</td>
<td>325-450</td>
</tr>
<tr>
<td>Ce₀.₅Zr₀.₅O₂</td>
<td>477</td>
<td>418-523</td>
</tr>
<tr>
<td>Ce₀.₈₅Fe₀.₁Zr₀.₀₅O₂</td>
<td>415</td>
<td>365-503</td>
</tr>
<tr>
<td>Ce₀.₇Fe₀.₁Zr₀.₂O₂</td>
<td>424</td>
<td>374-518</td>
</tr>
<tr>
<td>Ce₀.₆Fe₀.₁Zr₀.₃O₂</td>
<td>449</td>
<td>380-517</td>
</tr>
<tr>
<td>Ce₀.₅Fe₀.₁Zr₀.₄O₂</td>
<td>469</td>
<td>382-527</td>
</tr>
</tbody>
</table>

⁹ Temperature of maximum CO₂ concentration;
¹ Temperature range where 100 % NO conversion is completed.
Figure S1. (a) CO₂ concentration and (b) NO conversion of 3DOM Ce₀.₈₅Fe₀.₁Zr₀.₀₅O₂ catalysts fresh and aged at 800 °C for 5 h in air. After aging the catalyst was loosely mixed with Printex U model soot particles (reaction conditions: 1000 ppm NH₃, 1000 ppm NO, 3 % O₂ in N₂, model soot/catalyst mass ratio 0.1).
**Figure S2.** (a) CO₂ concentration and (b) NO conversion of 3DOM Ce₀.₈₅Fe₀.₁Zr₀.₀₅O₂ catalysts loosely mixed with Printex U model soot particles at various GHSV (reaction conditions: 1000 ppm NH₃, 1000 ppm NO, 3 % O₂ in N₂, model soot/catalyst mass ratio 0.1)
Figure S3. (a) CO$_2$ concentration and (b) NO conversion of 3DOM Ce$_{0.85}$Fe$_{0.1}$Zr$_{0.05}$O$_2$ catalysts (reaction conditions: GHSV = 25,000 h$^{-1}$, 1000 ppm NH$_3$, 1000 ppm NO, 3 % O$_2$ in N$_2$, model soot/catalyst mass ratio 0.1).
Figure S4. XRD patterns of 3DOM catalysts (a) CeO$_2$ (b) Ce$_{0.5}$Zr$_{0.5}$O$_2$ (c) Ce$_{0.85}$Fe$_{0.1}$Zr$_{0.05}$O$_2$ (d) Ce$_{0.7}$Fe$_{0.1}$Zr$_{0.2}$O$_2$ (e) Ce$_{0.6}$Fe$_{0.1}$Zr$_{0.3}$O$_2$ (f) Ce$_{0.5}$Fe$_{0.1}$Zr$_{0.4}$O$_2$

3DOM Ce$_{0.9-x}$Fe$_{0.1}$Zr$_x$O$_2$ catalysts exhibit typical diffraction peaks belonging to CeO$_2$, giving an indication that the dopant does not change the cubic structure of the catalysts. 3DOM Ce$_{0.9-x}$Fe$_{0.1}$Zr$_x$O$_2$ catalysts shows a little lower XRD peak intensity as compared to the pure 3DOM CeO$_2$, which is due to the dopant decrease the crystallinity. Concurrently, it is noted that the diffraction peaks of 2θ show a slight shift to high angle as compared to the counterpart pure 3DOM CeO$_2$ catalyst. It is mainly due to that the ionic radius of Fe$^{3+}$ or Zr$^{4+}$ is smaller than that of Ce$^{4+}$. In addition, the diffraction peaks of 3DOM Ce$_{0.85}$Fe$_{0.1}$Zr$_{0.05}$O$_2$ are the weakest and broadest among all 3DOM Ce$_{0.9-x}$Fe$_{0.1}$Zr$_x$O$_2$ samples.
Figure S5. \(\text{N}_2\) adsorption-desorption isotherms of 3DOM catalysts (a) \(\text{CeO}_2\) (b) \(\text{Ce}_{0.5}\text{Zr}_{0.5}\text{O}_2\) (c) \(\text{Ce}_{0.85}\text{Fe}_{0.1}\text{Zr}_{0.05}\text{O}_2\) (d) \(\text{Ce}_{0.7}\text{Fe}_{0.1}\text{Zr}_{0.2}\text{O}_2\) (e) \(\text{Ce}_{0.6}\text{Fe}_{0.1}\text{Zr}_{0.3}\text{O}_2\) (f) \(\text{Ce}_{0.5}\text{Fe}_{0.1}\text{Zr}_{0.4}\text{O}_2\)

All the isotherms are in coordination with the type II isotherm accompanied with the H3 hysteresis loop in the relative high pressure (\(P/P_0\)) range and a nearly linear correlation in the low pressure range. It is due to the unrestricted monolayer-multilayer adsorption. Whereas the appearance of the H3 hysteresis loop is an indication of the macroporous structure.\(^1\)\(^2\) With regard to 3DOM \(\text{Ce}_{0.9-x}\text{Fe}_{0.1}\text{Zr}_x\text{O}_2\) catalysts, it is noted that \(\text{N}_2\) uptakes increase slightly in the middle relative pressure of 0.4-0.8, showing the presence of the mesopores. A sharply increases of the H3 hysteresis loop in the \(P/P_0\) range of 0.8-1.0 of each sample is an indication of the macroporous structure.\(^3\)
Fig. S6 shows the representative TEM images of 3DOM catalysts (a) CeO$_2$ (b) Ce$_{0.85}$Fe$_{0.1}$Zr$_{0.05}$O$_2$ (c) Ce$_{0.7}$Fe$_{0.1}$Zr$_{0.2}$O$_2$ (d) Ce$_{0.6}$Fe$_{0.1}$Zr$_{0.3}$O$_2$ (e) Ce$_{0.5}$Fe$_{0.1}$Zr$_{0.4}$O$_2$

Fig. S6 shows the representative TEM images of 3DOM Ce$_{0.9-x}$Fe$_{0.1}$Zr$_x$O$_2$ catalysts. It is clearly seen from Fig. S6 that all the samples possess a high-quality 3DOM architecture interconnected by the macrospores, which is in accordance with SEM observations. The ordered macrospore permits the reactant with large sizes to enter their inner pores, which can improve the contact efficiency between reactant and catalyst. Thus, the perfect macroporous structure provides the ideal reaction place to PM emitted from diesel engines. After making a statistic analysis of the sizes of the samples, the measured interplanar acing could be obtained. From TEM images of CeO$_2$ sample (Fig. S6a), the measured interplanar acing is 0.31 nm, which belongs to the (111) crystal plane of the standard card for CeO$_2$. For the other 3DOM Ce$_{0.9-x}$Fe$_{0.1}$Zr$_x$O$_2$ catalysts, no other interplanar acing except that CeO$_2$ can be detected, which is corresponding well to XRD and Raman results.
Figure S7. TEM images of 3DOM Ce$_{0.85}$Fe$_{0.1}$Zr$_{0.05}$O$_2$ catalyst mixed with Printex U after temperature programmed oxidation until 250 °C (reaction conditions: GHSV = 25,000 h$^{-1}$, 1000 ppm NH$_3$, 1000 ppm NO, 3 % O$_2$ in N$_2$, model soot/catalyst mass ratio 0.1).
Figure S8. XPS curves of Ce3d, O1s for 3DOM catalysts (a) Ce$_{0.5}$Zr$_{0.5}$O$_2$ (b) Ce$_{0.85}$Fe$_{0.1}$Zr$_{0.05}$O$_2$ (c) Ce$_{0.7}$Fe$_{0.1}$Zr$_{0.2}$O$_2$ (d) Ce$_{0.6}$Fe$_{0.1}$Zr$_{0.3}$O$_2$ (e) Ce$_{0.5}$Fe$_{0.1}$Zr$_{0.4}$O$_2$
Figure S9. NH$_3$-TPD curves of 3DOM catalysts (a) CeO$_2$ (b) Ce$_{0.5}$Zr$_{0.5}$O$_2$ (c) Ce$_{0.85}$Fe$_{0.1}$Zr$_{0.05}$O$_2$ (d) Ce$_{0.7}$Fe$_{0.1}$Zr$_{0.2}$O$_2$ (e) Ce$_{0.6}$Fe$_{0.1}$Zr$_{0.3}$O$_2$ (f) Ce$_{0.5}$Fe$_{0.1}$Zr$_{0.4}$O$_2$
Figure S10. (A): In-situ DRIFT spectra of NH$_3$ desorption over 3DOM catalysts at 400 °C in the presence of 1000 ppm NH$_3$ (a) Ce$_{0.5}$Zr$_{0.5}$O$_2$ (b) Ce$_{0.85}$Fe$_{0.1}$Zr$_{0.05}$O$_2$ (c) Ce$_{0.7}$Fe$_{0.1}$Zr$_{0.2}$O$_2$ (d) Ce$_{0.6}$Fe$_{0.1}$Zr$_{0.3}$O$_2$ (e) Ce$_{0.5}$Fe$_{0.1}$Zr$_{0.4}$O$_2$ (B): In-situ DRIFT spectra of NH$_3$ desorption over 3DOM Ce$_{0.85}$Fe$_{0.1}$Zr$_{0.05}$O$_2$ catalysts in the presence of 1000 ppm NH$_3$ at different temperature

The in-situ DRIFT of NH$_3$ adsorption are detected to the change of acidity on the catalyst and presented in Fig.S10. The bands at 1065 and 1159 cm$^{-1}$ are related to the
coordinated NH$_3$ bound to Lewis acid sites, and the band at 1443 cm$^{-1}$ is attributed to the NH$^{4+}$ species on Brønsted acid. The bands at 1539 and 1342 cm$^{-1}$ are also observed. The former is attributed to the asymmetric bending vibration of N–H bond in –NH$_3^+$ group, which is generated from the decomposition of NH$^{4+}$ chemisorbed on a Brønsted acid site. The latter is related to scissoring and wagging vibrations of –NH$_2$ species, which is formed by hydrogen abstraction from NH$_3$ coordinated to a Lewis acid site. For 3DOM Ce$_{0.9-x}$Fe$_{0.1}$Zr$_x$O$_2$ catalysts, the Lewis, Brønsted acids as well as –NH$_3^+$ group and –NH$_2$ species can be detected, but for Ce$_{0.5}$Zr$_{0.5}$O$_2$ catalyst only the band ascribed to –NH$_2$ species are detected. The –NH$_3^+$ group is easy to combine with NO to produce NO$_3^-$, which is beneficial for PM combustion. It indicates that after the dopant of Fe, Ce-Zr mixed oxides is prone to produce more –NH$_3^+$ group.
Figure S11. In-situ DRIFT spectra over 3DOM catalysts in a flowing of 1000 ppm NO+ 3% O₂ at 400 °C (a) Ce₀.₅Zr₀.₅O₂ (b) Ce₀.₈₅Fe₀.₁Zr₀.₀₅O₂ (c) Ce₀.₇Fe₀.₁Zr₀.₂O₂ (d) Ce₀.₆Fe₀.₁Zr₀.₃O₂ (e) Ce₀.₅Fe₀.₁Zr₀.₄O₂
Reference:

